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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C04B 14/30, 14/34 // C09C 1/62</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/37386</b> <b>(43) International Publication Date:</b> 29 June 2000 (29.06.00)
<b>(21) International Application Number:</b> PCT/FI99/01057 <b>(22) International Filing Date:</b> 20 December 1999 (20.12.99)  <b>(30) Priority Data:</b> 982746 18 December 1998 (18.12.98) FI 982747 18 December 1998 (18.12.98) FI  <b>(71) Applicant (for all designated States except US):</b> OY CUSTONE LTD [FI/FI]; Ilmattarentie 13, FIN-00610 Helsinki (FI).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> MANNONEN, Risto, Olavi [FI/FI]; Päivänseläntie 1 C 9, FIN-02210 Espoo (FI). KORVENRANTA, Jorma, Artturi [FI/FI]; Hevoshaantie 5 A 6, FIN-01200 Vantaa (FI). LESKELÄ, Markku [FI/FI]; Rauduntie 19 D, FIN-02130 Espoo (FI). NÄSÄKKÄLÄ, Matti, Eerik [FI/FI]; Nahkahousuntie 6 B 36, FIN-00210 Helsinki (FI). KUKKONEN, Pertti, Juhani [FI/FI]; Ilmattarentie 13, FIN-00610 Helsinki (FI).  <b>(74) Agent:</b> LAITINEN, Pauli, S.; Patentti-Laitinen OY, P.O. Box 29, FIN-02771 Espoo (FI).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> <i>In English translation (filed in Finnish).</i>
<b>(54) Title:</b> METHOD FOR THE COLOURATION/INTENSIFICATION OF THE COLOUR OF CONCRETE  <b>(57) Abstract</b>  A method for the even and permanent coloration of concrete by adding a metal compound to the unset concrete being manufactured. The metal compound, especially a metal salt, is in an oxidized form when added and forms a pigment colouring the concrete only in reaction with compounds that have arisen during the hydration of the cement in the concrete, or which have dissolved from the atmosphere into the pore water of the concrete, or which have possibly been added to the concrete, to form a coloured compound with low solubility in water, and which colours the concrete. Alternatively, the metal is added both in a metallic form and as a salt.		

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## Method for the Colouration/Intensification of the Colour of Concrete

5 The present invention relates to a method for the coloration or alternatively the intensification of the colour of concrete.

Coloured concrete has been manufactured throughout the world for many years. The most typical coloured concrete products are paving slabs, roof tiles, concrete floors, or building facades. Traditionally, concrete has been coloured with inorganic pigments developed for this purpose. The pigments are normally fine-particle metal  
10 oxides. Iron oxides, which give concrete a red, black, yellow, or brown colour are the pigments that are most used and cheapest. Chrome oxide, which gives concrete a green colour, is clearly more expensive, while blue cobalt oxide is the most expensive of all concrete pigments. Typical dosages of metal oxides in concrete  
15 range from one to five percent by weight of the amount of the cement. In practice, this represents a total dose of 3 ... 20 kg of pigment /m<sup>3</sup> concrete.

Organic colours have also been experimented with in concrete, but the permanence of the colour is uncertain, especially outdoors. Similar reasons, have prevented the  
20 use of so-called soot-pigments in concrete products. Concrete technology textbooks always lay down at least the following requirements for pigments used in concrete:

- good resistance to cement and lime
- good resistance to weathering
- 25 - insolubility in water
- small particle size
- strong colouring effect
- even quality
- must not contain substances detrimental to the binding or hardening of cement

30 Particularly the first requirement of the pigment's chemical resistance to the alkali environment of concrete has been indisputable. This dominant alkali environment limits the use of all materials, including pigments, in concrete. The pH value of the pore water in concrete has been found to be as high as 14 in young concrete. This

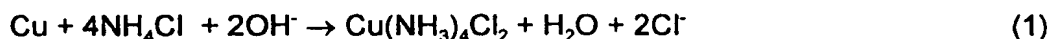
corresponds to the alkalinity of a four-percent solution in water of sodium hydroxide, i.e. lye. In all old concrete, and also in young concrete made from low-alkali cement, the pore water can be assumed to be saturated calcium hydroxide, with a pH value of about 12,7.

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Until recently, all methods for the integral colouring of concrete have had the characteristic that the intention is for the pigment or colour to remain in as precisely as possible the same chemical or physical form, in which it was when added to the concrete during manufacture. The method according to Patent FI 100398 B, in which

10 a metal reacts with a chemical added to the concrete to form a coloured compound, which then acts as a pigment, has opened an entirely new perspective on concrete colouring. One practical example of this is the reaction between metallic copper and ammonium chloride in an alkali environment.

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The final product of this series of reactions is blue copper hydroxide chloride, which is stable under the conditions in concrete. The weakness of this method is that at the same time as the complex according to reaction 1 arises, the metallic copper must oxidize to a valence of +2. The simplest way for this to take place is through the influence of atmospheric oxygen. Thus, colouring begins initially on the surface of the concrete, and only later in the interior of the concrete.

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In concrete technology, metal salts are used as additives. The most typical examples of the use of metal salts as concrete additives are:

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- The use of calcium chloride or formate as an accelerator
- The use of the sodium or calcium salts of naphthalene, melamine, or lignosulphonic acid as a plastizer
- The use of alkali salts of pinoline acids as a pore-forming agent
- The use of zinc hydroxide as a retardant
- The use of sodium nitrite or potassium carbonate as an additive to reduce the freezing point
- 35 - The use of sodium silicate or stearate as waterproofing agent

Other salts too have been used for various additive purposes, mainly to try to

influence either chemically or physically such properties of the unset concrete or the hardened concrete as the speed of the hydration of the cement, the water requirement of the unset concrete, or the surface tension or freezing point of the water in the unset concrete. The concrete's colour concrete has not been one of these properties.

The invention is intended to improve and facilitate the coloration properties of the methods disclosed above and to create a method for manufacturing coloured concrete so that it is strongly coloured immediately and the colour is made permanent, ensuring its evenness and permanence even over a long period, and otherwise simplifying and facilitating the manufacturing process.

These and other advantages and benefits of the invention are achieved in the manner described as characteristic in the accompanying Claims.

In the concrete colouring method according to the present invention, the colour of the concrete is created when metal compounds, such as metal salts, react with compounds formed in the hydration of the cement in the concrete, or with compounds formed as products of the reaction of gases dissolved from the atmosphere, to form colour particles with a low solubility in water. This means that the first and most important limitation in the foregoing list of requirements for pigments becomes the key to the invention. The concrete-colouring pigment forms in precisely these conditions.

However, if one wishes, the invention permits the use, of metals in an elemental form as a second colour-forming component, in which case the colour is not only formed in the above metal-salt reactions, but also when the metal reacts with compounds added for this purpose to the unset concrete, to form colour particles with low solubility in water.

Besides the aforementioned hydroxide ion, sulphates and various silicates, aluminates, and ferrites also arise in the hydration of cement. The most important compound from the air that dissolves in the pore water of the concrete is carbon dioxide, which appears as either a carbonate or hydrocarbonate ion, depending on the acidity of the water solution. Typically, coloured compounds with a low solubility arise when these ions react with transition metals, such as copper, cobalt, iron, or nickel.

The case according to reaction 3 can be used as a simple example of the concrete colouring method according to the invention, exploiting the reaction between copper chloride and the calcium hydroxide arising in the hydration of the cement:



As the reaction consumes the hydroxide ions that arise in the hydration of the cement, these may have to be added to the concrete during its manufacture. The same effect can be created by accelerating the hydration of the cement chemically with an appropriate accelerator. The metal salts to be added may also accelerate the hydration of the concrete, an effect that can be compensated with hydration-retardant additives.

When using a salt, no matter whether alone or in combination with a compound forming a metallic colour, the metal added as a salt to the concrete is already oxidized, so that the oxidation essential to form the colour of the metal is not required in the disclosed method.

According to this invention, a water-soluble salt is used as a sole or partial colour forming agent, so that a compound as a salt can be dissolved in the mix water prior to dosing. This method has the advantage that a colouring agent dissolved in the water does not increase the concrete's water requirement and that the reaction does not require the oxidation of the metal, such as copper, before the colour is formed. However, to ensure permanent colouring, it is highly recommended to use a metal in a metallic form.

Yet another significant benefit appears when the method is compared with colouring using traditional stable pigments. The use of such pigments to colour extensive concrete surfaces always results in a very uneven surface colour. This is because pigments in the form of solid particles generally join together in storage to form particles that are large compared to the original particle size. As the small particles usually do not separate from each other when concrete is made, the colouring effect of the pigment is reduced. This appears as colour variations between different manufacturing batches. When using a salt that is soluble or easily dispersed in water, the metal ions are evenly distributed in the pore water, with an equal number of colour particles forming throughout the concrete, giving a colour that is clearly more even.

- 5 The method according to the invention uses metal compounds, for instance a copper salt that is about 0,1 - 8 % by weight of the weight of the unset concrete. More usually the amount is about 0,5 - 5 % by weight, with the most probable amount used being about 1 - 3 % by weight. On the other hand, if metallic metal is used in addition to metal as a salt, these compound contents can be varied greatly, as required. The usual amount of the salt is 10 - 90 % of the total amount of the metal, preferably about 30 - 60 %.
- 10 Many different metal salts can be used, including chlorides, carbonates, nitrates, and sulphates.

Claims

1. A method for the coloration/intensification of the colour of concrete, to make it even and permanent, by adding metal compounds to the unset concrete during manufacture, **characterized** in that the metal compound is added either solely in an oxidized form, in which case it forms a pigment colouring the concrete only as the result of reactions taking place in the concrete, or the metal compound is added as a combination of the aforementioned oxidized form and the metallic form.
2. A method according to Claim 1, **characterized** in that the metal to be added in an oxidized form is a metal salt or a combination of metal salts, which react with compounds that have arisen during the hydration of the cement in the concrete, or which have dissolved from the atmosphere into the pore water of the concrete, or which have possibly been added to the concrete, to form a coloured compound with low solubility in water, and which colours the concrete.
3. A method according to Claim 1, **characterized** in that the metal compound or compounds, to be added in an oxidized form to the concrete, are water-soluble.
4. A method according to Claim 1, **characterized** in that a copper compound is added to the concrete and reacts with compounds arising in the hydration of the cement in the concrete, or which have dissolved from the atmosphere to the pore water of the concrete, or which have possibly been added to the concrete, to form a coloured compound with low solubility in water, and which colours the concrete.
5. A method according to Claim 4, **characterized** in that a copper salt is added to the concrete.
6. A method according to Claim 1, **characterized** in that a metal compound is used amounting to about 0,1 - 8 % by weight of the amount of unset concrete, preferably about 0,5 - 5 % by weight of the amount of unset concrete, at best about 1 - 3 % by



weight of the amount of unset concrete.

7. A method according to Claim 5, **characterized** in that the metal salt, especially a copper salt, is a chloride, carbonate, nitrate, or sulphate.

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8. A method according to Claim 1, **characterized** in that a metal salt is added to an amount of about 10 - 90 % of the total amount of metal to be added.

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9. A method according to Claim 1, **characterized** in that a metal salt is added to an amount of about 30 - 60 % of the total amount of metal to be added.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/FI 95/01057

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C04B 14/30, C04B 14/34 // C09C 001/62

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C04B, C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5401313 A (WILLIAM W. SUPPLEE ET AL), 28 March 1995 (28.03.95), column 2, line 47 - column 3, line 31, abstract --	1-9

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

25 April 2000

Date of mailing of the international search report

03 -05- 2000

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

02/12/99

International Application No.

PCT/FI 01057

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